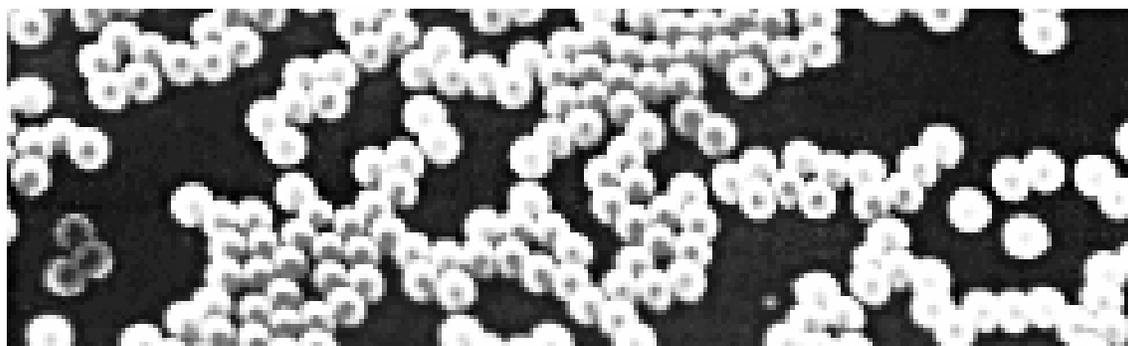


Characterization of Latex Microspheres with USANS

Summer School on Neutron Scattering and Reflectometry
From Submicron Structures
NIST Center for Neutron Research
June 6, 10-12, 2004

Abstract

Ultra-small-angle neutron scattering (USANS) will be used to determine the particle size, the polydispersity in size, and volume fraction of latex microspheres. The spheres size and polydispersity have been characterized separately by the manufacturer. All aspects of the experiment, from the sample preparation and instrument setup through to the data treatment and interpretation will be briefly described and references given for more in-depth study.



I. INTRODUCTION

Characterization of particle size is a common need in the field of materials science. Second phase dispersoids or voids in metal alloys or structural ceramics, and soft matter complexes such as oil-water emulsions have all been studied using small angle scattering. The much higher resolution of the new ultra-small-angle neutron scattering (USANS) instrumentation over conventional SANS extends the maximum particle size from 0.1 to 10 μm . The extension in the size range provides new opportunities of study not previously available.

Suspensions of nearly monodisperse colloidal particles offer many exciting scientific and industrial opportunities (Ottewill & Rennie, 1998). They are of interest not only because of their mesoscopic dimensions but also as promising systems from an applied point of view especially in optics. Since the particle size is well characterized by other methods, they are being used to test the size characterization capability of the USANS instrument.

Why use SANS?

Generally, static light scattering and small angle X-ray scattering (SAXS) provide the same information about the sample: measurement of macroscopic scattering cross-section $d\Sigma/d\Omega(q)$ as neutron scattering. The contrast in light scattering arises from the difference in the light's refractive index between the particle and water. The wavelength of light limits $q < 0.002 \text{ \AA}^{-1}$. The contrast in X-ray scattering arises from the variation in electron density. For the current latex colloid experiment, neutron, light or X-ray scattering could all be used for size characterization. The contrast for X-rays will be quite small due to similar electron densities of the phases. Static light scattering will require dilution of spheres to minimize multiple scattering.

We propose in this experiment to characterize the size of polystyrene particles in water. The spheres are certified by transmission electron microscopy (TEM) to have a mean diameter of $D = 499 \text{ nm} \pm 5 \text{ nm}$. The standard deviation in size obtained from measured size distribution was $\sigma = 6.5 \text{ nm}$. A nominal 1 volume % fraction of spheres is suspended in light water (H_2O), with a proprietary addition of surfactant to stabilize the suspension. To enhance the scattering contrast, the light water was replaced with heavy water (D_2O) by placing 8 ml of original sample in a resin bag, then allowing exchange with 400 ml of D_2O , yielding 98 % D_2O / 2 % H_2O mixture. During exchange, the volume fraction of spheres may have changed somewhat by change of volume of resin bag during exchange.

The Objectives of the Experiment are:

- **To determine the size and polydispersity of the dispersed particles.** This information will be derived from the shape, i.e. the q -dependence, of the scattering pattern. Since the particles are spherical, it will be necessary in order to characterize the size to measure the intensity over the range $1/D < q < 20/D$, where D is the average diameter of the particles.

- **Determine the volume fraction of the dispersed particles.** By integrating the scattering curve, we can determine a quantity called the Porod's invariant. The volume fraction can be determined from Porod's Invariant independent of particle volume. If the mean particle volume can be determined separately, the volume fraction can also be resolved from the $q \rightarrow 0$ limit of the scattering curve in absolute units.
- **Determine the surface area from the Porod regime.** The total surface area normalized by the sample volume can be determined from fitting the high Q regime.

II. PLANNING THE EXPERIMENT

Given the stated objectives of the experiment, how do we go about preparing for the experiment to maximize our chances of success? Here we discuss some of the issues that bear on this question.

II.1 Scattering Contrast

In order for there to be small-angle scattering, there must be scattering contrast between, in this case, the polystyrene latex particles and the surrounding water. The scattering is proportional to the scattering contrast, $\Delta\rho$, squared where

$$\Delta\rho = \rho_p - \rho_w \quad \leftarrow \text{Scattering Contrast} \quad (1)$$

and ρ_p and ρ_w are the **scattering length densities (sld)** of the particles and the water, respectively. Recall that **sld** is defined as

$$\rho = \frac{\sum_{i=1}^n b_i}{V} \quad \leftarrow \text{Scattering Length Density} \quad (2)$$

where V is the volume containing n atoms, and b_i is the (bound coherent) **scattering length** of the i^{th} atom in the volume V. V is usually the molecular or molar volume for a homogenous phase in the system of interest.

The **sld**'s for the two phases in the present case, polystyrene and water, can be calculated from the above formula, using a table of the scattering lengths (such as Sears,1992) for the elements, or can be calculated using the interactive *SLD Calculator* available at the NCNR's Web pages (<http://www.ncnr.nist.gov/resources/index.html>). The **sld**'s for polystyrene and water (both H₂O and D₂O) are given below in Table 1.

From Table 1 we see that scattering contrast for polystyrene in H₂O [proportional to $(1.41 - (-0.56))^2 = 3.88 \times 10^{20} \text{ cm}^{-2}$] is \sim six times smaller than in 98 % D₂O [$(1.41 - 6.24)^2 = 23.3 \times 10^{20} \text{ cm}^{-2}$]. By exchanging the particles from 100 % H₂O to 98% D₂O, the contrast was increased by a factor of six.

Table 1. The scattering length densities (SLD's) for polystyrene, light water and heavy water.

Material	Chemical Formula	Mass Density (g/cc)	SLD (cm ⁻²)
Polystyrene	C ₈ H ₈	1.05	1.41 x 10 ¹⁰
Light water	H ₂ O	0.998	-.56 x 10 ¹⁰
Heavy water	D ₂ O	1.107	6.38 x 10 ¹⁰

Sedimentation Mass density differences between the latex particles and the heavy water can cause the particles to float to top of container. Using Stoke's law, the velocity of sedimentation is proportional to the square of the diameter. For $D = 0.5 \mu\text{m}$, the separation process is slow enough for the planned experiment. For larger particles, or particles having a larger mass density difference with respect to the water such as silica, the samples must be continuously mixed. [For polystyrene, a mixture of 53 vol % H₂O / 47 vol % D₂O has the same mass density. But by matching the mass density, we would lower the scattering contrast by a factor of 14.]

II.2 Sample Thickness

The next decision we face is how thick should the sample be? Recall that the scattered intensity, $I(q)$, is proportional to the product of the sample thickness, d , and the sample transmission, T , where T , the ratio of the transmitted beam intensity to the incident beam intensity, is given by

$$T = e^{-\Sigma_t d}, \quad \Sigma_t = \Sigma_c + \Sigma_i + \Sigma_a \quad (3)$$

where the total cross section per unit sample volume, Σ_t , is the sum of the coherent, incoherent and absorption cross sections per unit volume. The absorption, or neutron capture, cross section, Σ_a , can be computed accurately from the tabulated absorption cross sections of the elements (and isotopes) if the mass density and stoichiometry of the phase is known. Σ_a is wavelength dependent, being linearly proportional to λ for nearly all elements. The incoherent cross section, Σ_i , can be *estimated* from the cross section tables for the elements as well, but not as accurately because it depends somewhat on the atomic motions and is, therefore, temperature dependent. The coherent cross section, Σ_c , is not easily estimated since it depends on the details of both the structure and correlated motion of the atoms in the material. The scattering from H₂O is dominated by incoherent scattering, whereas D₂O has significant contributions from incoherent and coherent scattering. Table 2 gives the measured total cross-sections for H₂O and D₂O at $\lambda = 2.38 \text{ \AA}$.

Table 2. Macroscopic cross sections (i.e. total cross section per unit volume) for light and heavy water measured on the USANS at wavelength of 2.38 Å.

Material	Σ_t (cm ⁻¹)	1/ Σ_t (cm)
Polystyrene	~4	0.24
H ₂ O	4.1	0.24
D ₂ O	0.5	2.0

The sample to be measured consists of approximately 1 vol % polystyrene in 98 vol % D₂O/ 2 % H₂O solution. Hence the total cross section per unit volume for the suspension is $0.99 [(0.98 \times 0.5 \text{ cm}^{-1}) + (0.02 \times 4.1 \text{ cm}^{-1})] + 0.01 (4 \text{ cm}^{-1}) = 0.61 \text{ cm}^{-1}$, and $1/\Sigma_t = 1.6 \text{ cm}$. Hence the optimal sample thickness¹, the 1/e thickness, is 1.6 cm. The corresponding thickness for the same volume fraction of polystyrene in H₂O is 0.24 cm. By redispersing the spheres in D₂O instead of H₂O, we are able to increase the scattered signal by utilizing a thicker sample.

Multiple scattering The scattered intensity is proportional to $d \exp(-\Sigma_t d)$ which has a maximum at $d = 1/\Sigma_t$. But if the small-angle scattering (SAS) intensity is strong enough to create multiple scattering, the scattering curve will become distorted in shape (Schelten & Schmatz, 1980). The sample thickness t should then be chosen to make transmission from only SAS to be $T_{\text{SAS}} = \exp(-\Sigma_{\text{SAS}} t) > 0.9$ rather than $1/e = .37$ to avoid multiple scattering. The cross-section due to SAS can be calculated for monodisperse spheres as

$$\Sigma_{\text{SAS}} = \frac{3}{4} \lambda^2 \phi \Delta\rho^2 D \quad (4)$$

where ϕ is the volume fraction and D is the sphere diameter. For the current sample using nominal volume fraction $\phi \approx 0.01$, $\Sigma_{\text{SAS}} \approx 0.5 \text{ cm}^{-1}$. By using a thinner ($t = 0.1 \text{ cm}$) sample, multiple scattering is minimized, with $T_{\text{SAS}} \approx 0.95$.

II.3 Required Q-Range

For this experiment we know we will need to measure the intensity over a wide q -range since the information we are looking for is distributed in the low and high q regime. To get a better idea of the required q -range, we can use the *SANS Data Simulator* (<http://www.ncnr.nist.gov/resources/simulator.html>) to calculate the Q -dependence of the scattering for the case of non-interacting polydisperse spherical particles. From among the 20 different particle models currently included in the *SANS Data Simulator*, we choose the *Polyhardsphere* model. The documentation for this model can be found on the Web site at <http://www.ncnr.nist.gov/resources/sansmodels/polyhardsphere.html>. A plot from the *SANS Data Simulator* for 1 vol % spheres with polydispersity ($p = \sigma/D$) in sphere diameter of $p = 0, 1.3\%$ and 5% are shown in Figure 1. Note how with increasing polydispersity, the minima in scattering function are attenuated. Determination of the polydispersity from SAS data requires accurate measurement of the oscillating section of scattering curve.

III. COLLECTING THE DATA

Figure 2 shows the schematic layout of the instrument. The sample is placed in a two-position sample changer. A channel cut silicon crystal (monochromator) provides a neutron beam onto the sample with excellent angular collimation (2 arcsec) in the horizontal direction, but with poor resolution in the vertical direction. To select a scattering angle, a second channel-cut silicon crystal (analyzer) is rotated. The main

detector than collects scattering with high resolution in horizontal direction. Figure 3 represents the q-resolution obtained using the USANS double crystal diffractometer.

III.1 How to Configure the USANS Instrument

The USANS instrument collects data at one value of q at a time. Thus, we need to choose all the q-values to count during the experiment. Since we need to cover an extended Q-range, $5 \times 10^{-5} \text{ \AA}^{-1} < q < 5 \times 10^{-3}$, we break the data collection into six separate equally spaced scans, with each subsequent scan having roughly doubled q-spacing. The first scan spans the main beam. The peak intensity is used to determine the q=0 orientation, scales the intensity into absolute units, and determines the sample transmission.

III.2 Sample Transmission

The sample transmission is determined in two ways. A separate transmission detector (see figure 2), located behind the analyzer, collects all neutrons transmitted through the analyzer. When the analyzer is rotated a sufficient angle off of main beam orientation, the transmission detector collects both the direct beam intensity, and the small angle scattered intensity. The ratio of counts collected with the transmission detector, with and without the sample, is the sample transmission (T_{wide}) due to attenuation from incoherent scattering and absorption. In addition, rotating the analyzer through the orientation of the main beam measures only the beam intensity in the main detector. Thus the peak intensity measured with the sample measures the transmission (T_{rock}) of the sample due to attenuation from incoherent scattering, absorption and *small angle (coherent) scattering*. The ratio of these separate transmission measurements can be used to estimate the amount of multiple scattering by determining the scattering power ($\tau = \Sigma_{\text{SAS}}$) by

$$T_{\text{SAS}} = \frac{T_{\text{Rock}}}{T_{\text{Wide}}} = e^{-\tau} \quad (5)$$

III.3 What Measurements to Make

To correct for instrument “background”, measurement of the scattering without the sample is needed. Counts recorded by the detector with the sample in place can come from three sources: 1) neutrons scattered by the sample itself (the scattering we are interested in); 2) neutrons scattering from something other than the sample, *but which pass through the sample*; and, 3) everything else, including neutrons that reach the detector *without passing through the sample* (stray neutrons or so-called room background) and electronic noise in the detector itself. To separate these three contributions, we need three measurements:

- i) Scattering measured with the sample in place (which contains contribution from all 3 sources listed above), denoted \mathbf{I}_{sam} ;
- ii) Scattering measured with the empty sample holder in place (which contains contributions from the 2nd and 3rd sources listed above), denoted \mathbf{I}_{emp} ; and,

iii) Counts measured with a complete absorber at the sample position (which contains only the contribution from the 3rd source listed above) denoted I_{bgd} .

The I_{bgd} on the USANS instrument is due predominantly to fast neutrons. This background is independent of instrument configuration and is $0.018 \text{ s}^{-1} = 0.62 / 10^6$ monitor counts. For this reason, separate beam blocked runs are generally not made for the USANS instrument.

III.4 How Long to Count

A SANS experiment is an example of the type of counting experiment where the uncertainty, or more precisely the standard deviation, σ , in the number of counts recorded in time, $I(t)$, is $\sigma = \sqrt{I(t)}$. Increasing the counting time by a factor of four will reduce the relative error, σ/I , by a factor of two. If there are 1000 total counts per data point, the standard deviation is $\sqrt{1000} \sim 30$, producing an relative uncertainty of about 3 %, which is good enough for most purposes.

A related question is how long should the empty cell measurements be counted relative to the sample measurement. The same $\sigma = \sqrt{I(t)}$ relationship leads to the following approximate result for the optimal relative counting times

$$\frac{t_{background}}{t_{sample}} = \sqrt{\frac{Count\ Rate_{background}}{Count\ Rate_{sample}}} \quad (6)$$

Hence if the scattering from the sample is weak, the background should be counted for as long (but no longer!) as the sample scattering. However, if the sample scattering count rate is, say, 4 times greater than the background rate, the background should be counting only half as long as the sample scattering.

Since the scattering usually becomes much weaker at larger q , the time spent per data point is greatly increased with higher q scans.

IV. DATA REDUCTION

Data reduction consists of correcting the measured scattering from the sample for the sources of background discussed in Section III.3, and rescaling the observed corrected data on an absolute scale of scattering cross section per unit volume. The scaling of the slit smeared background-corrected neutron count rate, $I_{cor}(q)_S$, to the slit smeared absolute cross section, $d\Sigma_S(q)/d\Omega$, is done through the expression

$$I_{cor}(q)_S = \varepsilon I_{Beam} \Delta\Omega_A d T (d\Sigma_S(q)/d\Omega) \quad (7)$$

Where:

ε = detector efficiency.

I_{beam} = The intensity of the beam incident upon sample (neutrons/sec)

d = the sample thickness

T = the transmission of the sample (and its container, if there is one)
 $\Delta\Omega$ = the solid angle accepted by analyzer
 $d\Sigma_S(q)/d\Omega$ = slit smeared scattering cross-section.

The beam intensity, $\varepsilon I_{\text{Beam}}$, is measured by rotating analyzer through the direct beam at $q = 0$ with the empty cell in the beam. The transmission T is measured by taking the ratio of count rate obtained with and without the sample in the beam with transmission detector. The solid angle of scattering collected by the analyzer is

$$\Delta\Omega_A = \left(\frac{\lambda}{2\pi}\right)^2 (2\Delta q_V)\Delta q_H, \quad (8)$$

where $2\Delta Q_V$ is the total vertical divergence of the beam determined from the size and geometry of the instrument and Δq_H is the horizontal divergence accepted by diffraction of monochromator and analyzer crystals. The instrument accepts scattered neutrons with a vertical acceptance of $\pm 1.1^\circ$, producing $\pm \Delta q_V = 0.037 \text{ \AA}^{-1}$ divergence in terms of momentum transfer q . The horizontal resolution Δq_H is measured from the full width at half maximum (fwhm) of the main beam profile obtained by rotating analyzer through direct beam. The fwhm is 2.00 arcsec, producing $\Delta q_H = 2.55 \times 10^{-5} \text{ \AA}^{-1}$. The solid angle accepted by the analyzer is $\Delta\Omega_A = 2.7 \times 10^{-7} \text{ Ster}$.

Smearing

The analyzer has good resolution in only one direction, as shown in figure 3. The measured smeared cross-section $d\Sigma/d\Omega_S(q)$ is related to desired true cross-section $d\Sigma/d\Omega(q)$ by the relation (Roe, 2000)

$$\frac{d\Sigma_S}{d\Omega}(q) = \frac{1}{\Delta q_V} \int_0^{\Delta q_V} \frac{d\Sigma}{d\Omega} \left(\sqrt{q^2 + u^2}\right) du \quad (9)$$

Figure 4 shows the slit-smeared scattering from spherical particles having $\phi = 0.01$ with $p = 0.0, 0.13$ and 0.05 . Compare this to the 'true' scattering shown in figure 1. Infinite slit smearing tends to dampen the oscillations. Desmearing the data directly can be done by an iterative convergence method (Lake, 1967). The desmeared result is very unstable, being sensitive to noise in the data. In our analysis we will fit the smeared data *directly*.

V. DATA ANALYSIS

V.1 Modeling the Scattering

Since the volume fraction of the spherical polystyrene particles in our sample is about 0.01, it is reasonable to analyze the scattering in terms of non-interacting particles. For higher volume fractions, the correlation in particle positions must be considered. Exclusion of possible positions due to impenetrability of the hard spheres can be modeled by Percus & Yevick, 1958. Charge stabilization can cause larger effects at even relatively dilute concentrations (Chen & Lin, 1987). In the so-called dilute limit, the

particles scatter independently, and the total scattering is the sum of the scattering from each particle. The measured intensity (corrected for background and put on an absolute scale) for monodisperse spherical particles can be expressed as

$$\frac{d\Sigma(q)}{d\Omega} = \Delta\rho^2 \langle V_p^2 \rangle N_p P(q), \quad (10)$$

where $\Delta\rho$ is the difference in sld's between the polystyrene particles and D_2O ; $\langle V_p^2 \rangle$ is the mean particle volume squared, and N_p is the number of particles per unit volume. $P(q)$ is the scattering form factor, which for spherical particles is

$$P(q, R) = \left| \frac{1}{V_p} \int_{V_p} e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} \right|^2 = \left[\frac{3(\sin qR - qR \cos qR)}{(qR)^3} \right]^2 \quad (11)$$

where R is the sphere radius. The scattering from a size distribution $f(R)$ of particles is

$$\frac{d\Sigma(q)}{d\Omega} = \left(\frac{4\pi}{3} \right)^2 \Delta\rho^2 N_p \int f(R) R^6 P(q, R) dR \quad (12)$$

Since the current sample is relatively monodisperse, we will approximate the shape of the distribution with a gaussian:

$$f(R) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2\sigma^2} (R - R_{avg})^2\right] \quad (13)$$

where R_{avg} is the mean particle radius. We define $p = \sigma / R_{avg}$. Figure 5 shows the number density distribution for two different polydispersity $p = 0.13$ (our sample) and $p = 0.05$, used to calculate the scattering in figure 1.

V.2 Particle Volume Fraction Determined from Invariant

For all two phase systems having uniform scattering length densities in each phase, the volume fraction ϕ can be determined from the integration of the scattering

$$\phi(1 - \phi) = \frac{Q_I}{2\pi^2 \Delta\rho^2} \quad (14)$$

where the invariant is determined by

$$Q_I \equiv \int_0^\infty q^2 \frac{d\Sigma}{d\Omega}(q) dq \cong \frac{1}{\Delta q_v} \int_0^\infty q \frac{d\Sigma_s}{d\Omega}(q) dq \quad (15)$$

Figure 6 shows an *invariant* plot of the slit-smear scattering: $qI_s(q)$ vs q . By integrating the area under the curve, we will be able to determine the Porod invariant Q_I

and subsequently the volume fraction ϕ . This technique of determining the volume fraction from scattering data works regardless of particle shape.

V.3 Particle Volume Fraction Determined from Forward Scattering

For dilute systems, and if the particle has a uniform scattering length density, the forward scattering is simply:

$$\frac{d\Sigma}{d\Omega}(0) = N_P \langle V_P^2 \rangle \Delta\rho^2 = \frac{4}{3} \pi \phi \Delta\rho^2 \frac{\langle R^6 \rangle}{\langle R^3 \rangle} = \frac{4}{3} \pi \phi \Delta\rho^2 R_{avg}^3 \frac{(1 + 15p^2 + 45p^4 + 15p^6)}{(1 + 3p^2)} \quad (16)$$

where ϕ is the volume fraction of particles, V_P is the average particle volume, and $\Delta\rho^2$ is the scattering length density contrast squared. By slit-smearing Guinier approximation, we can estimate the forward scattering $d\Sigma/d\Omega(0)$ directly from slit smeared intensity by

$$\frac{d\Sigma}{d\Omega}(0) \approx \frac{2R_G \Delta q_V}{\sqrt{3\pi}} \frac{d\Sigma_S}{d\Omega}(0) \quad (17)$$

Since we know R_{avg} , p , and $\Delta\rho$, and $d\Sigma/d\Omega(0)$ from equation 17, we can determine the volume fraction ϕ . We will determine $d\Sigma_S/d\Omega(0)$ by performing a Guinier fit, described later in section V.5.

V.4 Determination of the Interfacial Surface Area:

Total interfacial surface area is determined from small angle scattering data using Porod's asymptotic approximation:

$$\lim_{q \rightarrow \infty} \frac{d\Sigma}{d\Omega}(q) \equiv C_P / q^4 = 2\pi \Delta\rho^2 S / q^4 \quad (18)$$

where S is the interfacial surface area per unit sample volume. The slit smeared intensity in the Porod region is modeled as

$$\lim_{q \rightarrow \infty} \frac{d\Sigma_S}{d\Omega}(q) \equiv C_{P,S} / q^3 = \frac{\pi C_P}{4\Delta q_V q^3} \quad (19)$$

For a Gaussian distribution of sizes

$$S = 4\pi \langle R^2 \rangle N_P = 3\phi \frac{\langle R^2 \rangle}{\langle R^3 \rangle} = \frac{3\phi}{R_{avg}} \frac{(1 + p^2)}{(1 + 3p^2)} \quad (20)$$

Figure 7 shows the slit-smearing Porod plot: $q^3 I(q)$ vs q . By determining an average value between oscillations, we can determine $C_{P,S}$, C_P and subsequently S . Using equation 20, we can then determine the volume fraction ϕ .

V.5 Determination of Particle size from Guinier Law:

In the Guinier limit $q \rightarrow 0$, the above expressions 8-10 simplify to

$$\frac{d\Sigma}{d\Omega}(q) = \frac{d\Sigma}{d\Omega}(0)\exp(-q^2 R_g^2 / 3)$$
$$R_G = \sqrt{\frac{3\langle R^8 \rangle}{5\langle R^6 \rangle}} = R_{avg} \sqrt{3/5} \frac{(1 + 28p^2 + 210p^4 + 420p^6 + 105p^8)}{(1 + 15p^2 + 45p^4 + 15p^6)} \quad (21)$$

The above equation is an example of Guinier's Law which is valid only for $q R_g \leq 1$, where R_g is the radius of gyration of the particle. **For a homogenous sphere, $R_g^2 = 3R^2/5$.** This expression is easy to use and allows us to quickly extract the radius of gyration of particles in the low q region by plotting $\ln(I)$ versus q^2 . Figure 8 shows the scattering using a Guinier plot. Note that slit smearing does not change the slope of curve, but shifts the curve vertically according to equation 17.

V.6 Summary of Analysis Tasks

We shall perform the following fits to the slit smeared scattering $d\Sigma_S/d\Omega(q)$ data:

- 1) Use a Gaussian shaped size distribution of spheres to determine mean sphere size R_{avg} , the polydispersity P and the volume fraction ϕ . Equations 10-13 are used.
- 2) Integrate the scattering according to equation 15 to determine Porod's invariant Q_I . The invariant will be used to determine the volume fraction ϕ using equations 14 and 15.
- 3) Perform a Guinier fit to the data as shown in figure 8. The slope will be converted to a Guinier radius R_G which can then be used to calculate the mean particle radius R_{avg} . The forward cross-section, corrected for smearing by equation 17, will be used to calculate the volume fraction ϕ .
- 4) Make a Porod plot and determine asymptotic Porod's constant $C_{P,s}$. From equations 18 and 19 determine interfacial surface area S . From know average particle size, determine volume fraction using equation 20.

From the above fits, we will have one determination of polydispersity P , two determinations of mean particle size R_{avg} , and four separate determinations of volume fraction.

VI. REFERENCES AND OTHER RESOURCES

- Chen, S.-H. & Lin, T.-L. *Methods of Experimental Physics*, **23B**, 489-543 (1987).
Lake, J. *Acta Cryst.*, **23**, p191-194 (1967).
Ottewill, R.H. & Rennie, A.R. *Modern Aspects of Colloidal Dispersions*, Kluwer Academic Publishers (1998).
Percus, J.K. & Yevick, G.J. *Phys. Rev.* **110**, 1-13 (1958)..
Roe, R.J. *Methods of X-Ray and Neutron Scattering in Polymer Science*, Oxford University Press, (2000).
Schelten, J. & W. Schmatz, *J. Appl. Cryst.* **13**, p385-390 (1980).
Sears, V.F. *Neutron News*, **3**, No. 3, p 26 (1992).

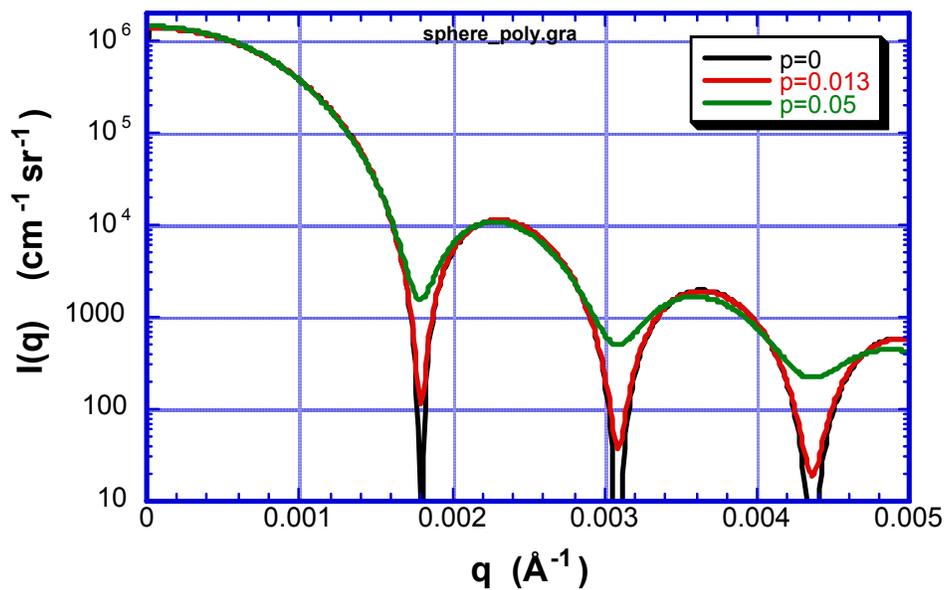


Figure 1. The simulated SANS from polydisperse spheres with diameter $D = 5000 \text{ \AA}$. Three different polydispersities are included ($P = 0$ (monodisperse), 1.3 % and 5 %).

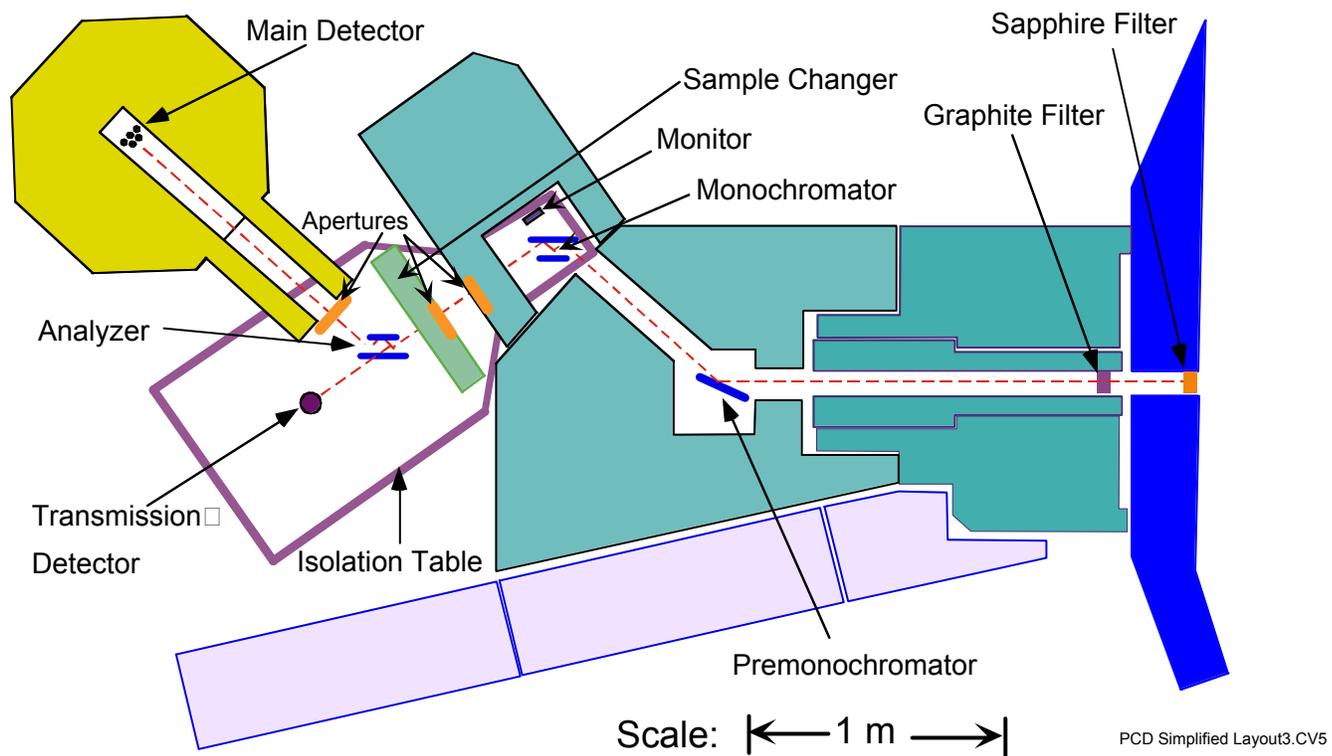


Figure 2. Figure of the schematic layout of the USANS instrument. The dashed line indicates the beam path. The measured scattering angle, or momentum transfer q , is determined by rotation of analyzer crystal.

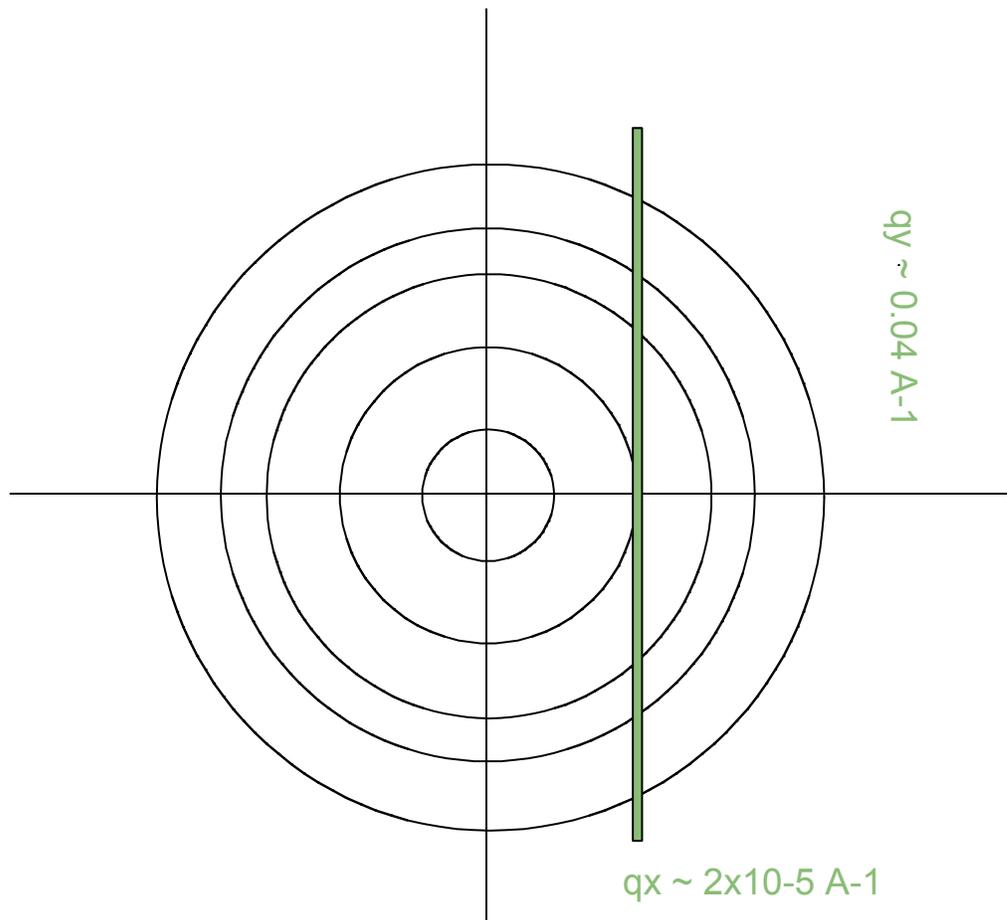


Figure 3. View of scattering with axis q_x and q_y collected by analyzer on USANS instrument. Circles represent iso-intensity contours from isotropic small angle scattering. The narrow slit represents the scattering region collected by analyzer.

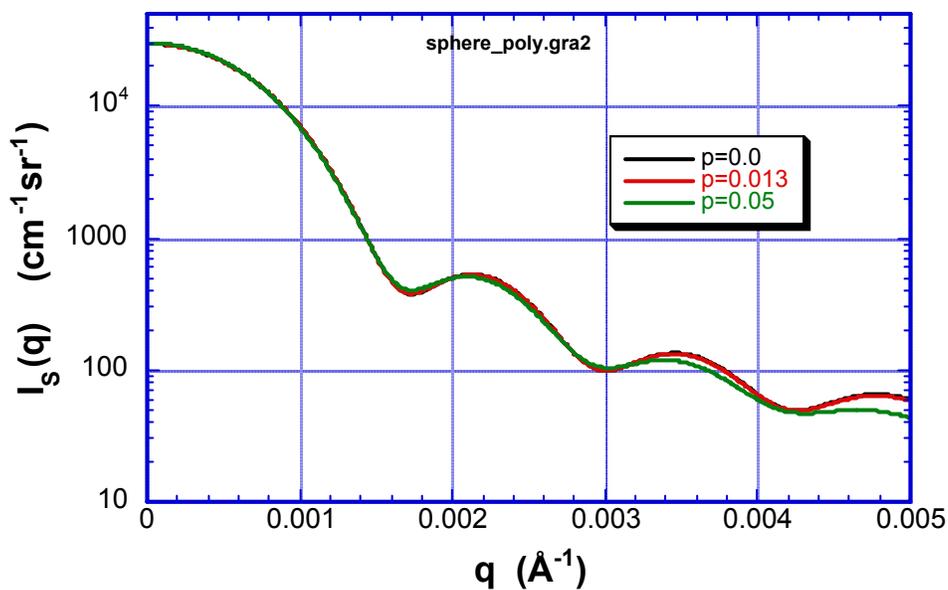
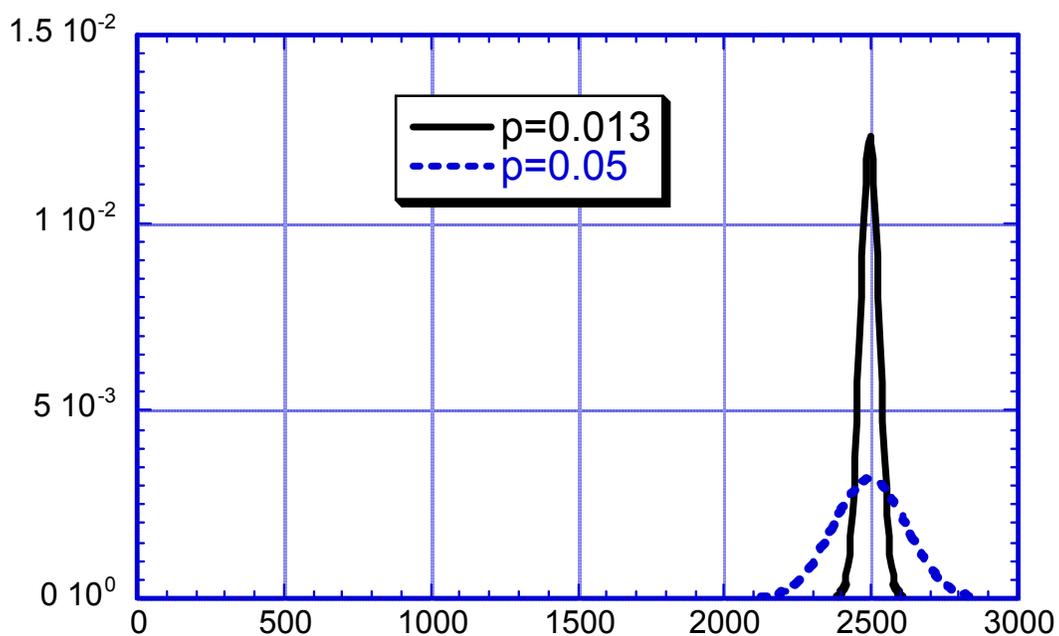


Figure 4. Slit smeared scattering cross-section for spherical particles, $R_{\text{avg}}=2495 \text{ \AA}$, for



polydispersity $p=0, 0.013$ or 0.05 . The slit length for smearing was $\Delta q_v = 0.037 \text{ \AA}^{-1}$. **Figure 5.** Plot showing the distribution in sizes corresponding to polydispersity index $p = 0.013$ and 0.05 . The vendor's size characterization has $p=0.013$ for the latex sample.

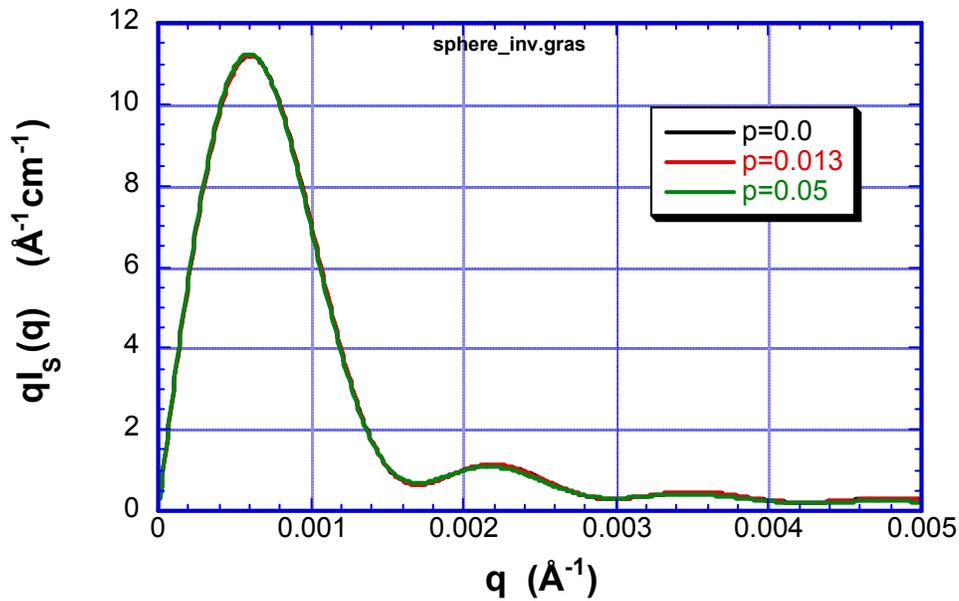


Figure 6. Invariant type plot of slit smeared data: $qI_s(q)$ vs q . The area under curve is proportional to the Porod invariant Q_I which can be used to calculate volume fraction.

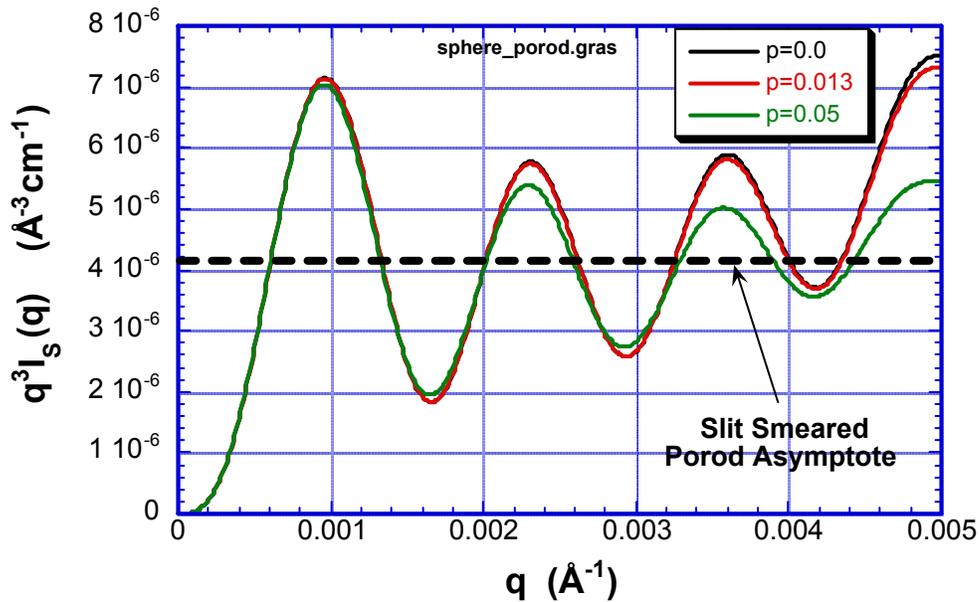


Figure 7. Porod type plot of slit smeared data: $q^3 I_s(q)$ vs q . The dashed curve is the average value of asymptotic data: $C_{P,S}$.

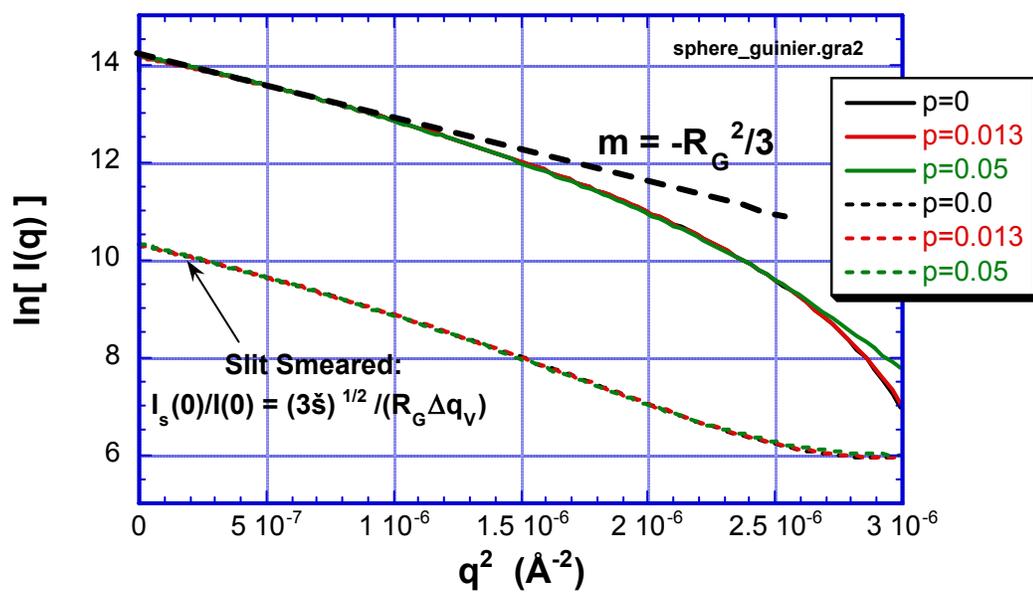


Figure 8. Plot showing Guinier fit to model data [$\ln(I)$ vs. q^2]. Fit made in small q limit: $0 < q < 1.2/R_G$. Dashed curves show effect of slit smearing.